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THIN COPPER, GOLD, AND ALUMINUM FILMS ON SILICATE GLASS

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The composition and structure of thin copper, gold, and aluminum films deposited on a substrate made of vitreous quartz are investigated. The composition of the film – substrate interfaces is analyzed.

Thin metal films are applied on silicate glass for various purposes: for instance, to produce glasses and decorative coatings, to make large and superlarge integrated circuits. The latter are based on metal – oxide – semiconductor structures, in which silicon is the most frequently used semiconductor, silicon dioxide serves as a substrate, and aluminum, gold, silver, and nickel are used as metals.

The processes of interaction between the metallic film and the silicon oxide substrate are not sufficiently studied. The reaction of precipitated metal with the gaseous phase, which should be taken into account even in vacuum, can have a significant effect on these processes. The interaction of metal with oxide can be estimated using what is known as Ellingham's diagrams, which are graphic representations of the temperature dependences of variations in the Gibbs free energy of oxide formation from elements (Fig. 1) [1]. At the same time, Ellingham's diagram does not allow for identification of the system components.

The purpose of our work was to study the composition and structure of thin films of copper, gold, and aluminum deposited on a vitreous quartz substrate.

Thin copper and gold films were spray-deposited by the thermovacuum method in the preparation chamber of a ÉS-2401 spectrometer in vacuum of 10^{-8} Torr. Their thickness was determined based on the time of pickling using argon ions (1 keV) with known pickling rate.

The aluminum films were obtained by magnetron spraying on a VATT 17600-3M plant. The sprayed target (Al) moves along the glass surface and serves as the cathode, to which a negative potential is supplied (about 400 V). The second electrode is the chamber body. Spraying is implemented in an argon atmosphere under a pressure of 10^{-5} Pa.

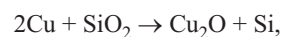
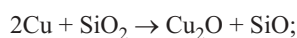
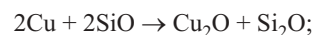
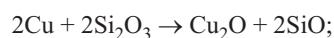
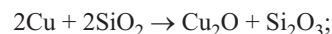
The x-ray studies were implemented using an upgraded ES-2401 electron spectrophotometer [2]. The spectra were excited by MgK_{α} radiation. The spectra were processed according to the method described in [3].

The surface topography was studied using atomic force microscopy employing a R-47 scanning probe microscope in the semicontact mode in air.

Gold films. The free energy of the formation of gold oxide is not indicated in Fig. 1. It is higher than that of silicon oxide and has a positive sign up to high temperatures. Hence it follows that the emergence of thermodynamically stable compounds on the gold – silicon dioxide interface is virtually impossible. Indeed, gold introduced into glass in melting exists in the atomic state of various degrees of dispersion, and in ruby with glass impurities it is observed in the forms of crystalline particles, which have a cubic shape and impart a red or a blue tint to the glass depending on their sizes.

Table 1 lists the compositions of investigated films. The Au4f line in a gold film 10–12 nm thick line has a position corresponding to metallic gold. Oxygen and silicon components that are part of silicon dioxide are distinguished in the Si2p and O1s spectra. The components correlated to silicon and oxygen are not registered in the silicon-oxygen anions bonded with metal. This is evidence that gold does not chemically react with quartz glass.

Copper film. It was assumed in [4] that the following reactions take place at the SiO_2 – Cu interface:



and the authors conclude that by varying the spraying duration one can avoid the formation of undesirable compounds (SiO and copper oxides) on the surface.

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Since the probability of the specified reactions contradicts the data of Ellingham's diagram, the heterogeneous equilibrium of the SiO_2 – Cu – gas system was calculated in [5] for a substrate temperature of 300 – 1300 K and a total pressure in the reaction chamber equal to 10^{-4} – 10^{-5} Pa. Two variants were calculated. The first is an ideal variant, in which oxygen is completely absent in the gaseous phase. The second is a realistic variant assuming the possibility of the presence of oxygen partly dissolved in metal, adsorbed on the vacuum chamber walls, or penetrating into the vacuum chamber via sealings. In the ideal variant the formation of any oxide phases is shown to be impossible up to a temperature of 1050 K. Above this temperature, thermal dissociation of silicon dioxide starts. Precipitation of copper on the substrate ends at a temperature above 1300 K, since the equilibrium pressure of copper vapor above the substrate exceeds the pressure of the evaporation source. The calculations of the first variant demonstrated that the above listed solid-phase reactions are impossible in the conditions of the experiment [4].

In the real variant, CuO and Cu_2O precipitate on the substrate in the ratio of 1 : 5 within a temperature range of 300 – 600 K. It is assumed that copper silicate Cu_2SiO_4 is formed as well, similarly to nickel silicate [5]. Crystalline anhydrous copper silicates have not yet been obtained. However, it has been possible to obtain amorphous copper silicate [6], whose composition is close to diorthosilicate, using the sol-gel method in the temperature range of 830 – 970°C. It is assumed that by modifying the conditions of synthesis and annealing, it is possible to obtain crystalline copper orthosilicate. Additional calculations carried out by us showed that at 300 – 500 K copper in the film virtually does not react with silicon oxide, and the formation of impurities (here and elsewhere molar content) of Cu_2O (about $10^{-3}\%$) and CuO (about $10^{-5}\%$) is mainly due to the reaction of copper with oxygen of the gaseous phase.

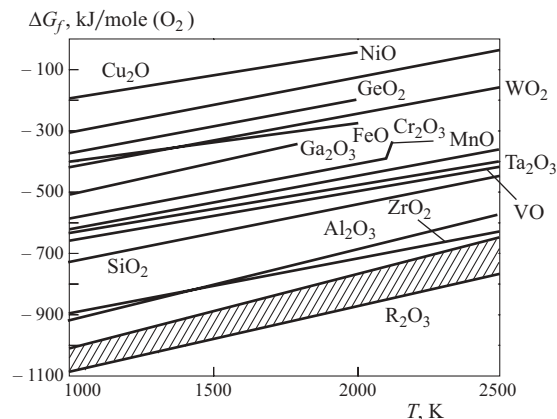


Fig. 1. Ellingham's diagram.

CuO and copper silicate components are registered in the x-ray-electron The Cu2p spectra. Cu2p lines from non-oxidized copper and from copper in Cu_2O have the same position. The presence of Cu_2O is indicated by a satellite line shifted to a distance of 6 eV (toward higher bond energy) from the main line.

The O1s spectrum exhibits components produced by oxygen contained in copper oxides and copper silicate. It can be assumed that an amorphous phase of copper silicate is formed in thermovacuum spraying of copper.

Aluminum films. Metals, whose free energy of oxide formation is lower than that of SiO_2 , can directly reduce silicon dioxide. According to the data in Fig. 1, aluminum (same as zirconium and rare-earth metals) is such a metal.

To analyze the compositions of precipitated films, thermodynamic calculations of equilibrium characteristics were performed for the multi-component heterogeneous system SiO_2 – Al – air according to the method described in [7] based on finding the extremum of the system entropy subject to satisfying several boundary conditions and implemented

TABLE 1

Sample	Thickness, nm	Silicon		Oxygen		Metal	
		chemical bond	atomic content, %	chemical bond	atomic content, %	chemical bond	atomic content, %
Au/ SiO_2	10 – 12	Si – O(SiO_2)	28.30	O – Si(SiO_2)	60.90	Au ⁰	10.90
Cu/ SiO_2	10 – 12	Si – O(SiO_2)	2.00	O – Si(SiO_2)	4.80	Cu ⁰	33.40
		Si – O – Cu	10.30	O – Cu(CuO)	10.80	CuO	8.20
				O – Cu(Cu_2O)	2.80	Cu_2O	6.00
				O – Si – Cu	18.80	Cu – O – Si	2.90
Cu/ SiO_2	2 – 5	Si – O(SiO_2)	8.00	O – Si(SiO_2)	22.50	Cu ⁰ + Cu_2O	1.90
		Si – O – Cu	9.80	O – Cu(CuO)	4.29	Cu – O(CuO)	3.80
				O – Si – Cu	33.80	Cu – O – Si	7.00
				O – Si(SiO_2)	9.30	Al ⁰	10.10
Al/ SiO_2	120	Si ⁰	1.10	O – Al(Al_2O_3)	18.50	Al – O	9.60
		Si – O(SiO_2)	4.30	O – Al – Si	31.80	Al – Si – O	11.00
		Si – O – Al	4.00	O – Si(SiO_2)	2.10	Al ⁰	19.00
Al/ SiO_2	300	Si ⁰	0.15	O – Al(Al_2O_3)	26.90	Al – O	15.00
		Si – O(SiO_2)	0.92	O – Al – Si	23.10	Al – Si – O	8.00
		Si – O – Al	1.72				

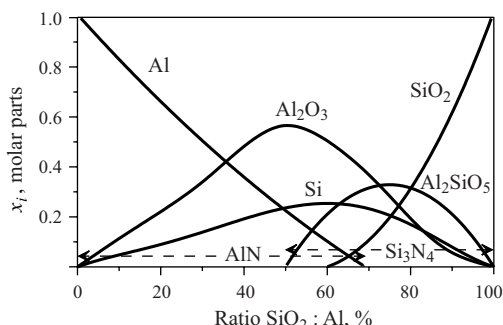


Fig. 2. Content of components in the condensed phase x_i depending on the ratio $\text{SiO}_2 : \text{Al}$ in air – Al – SiO_2 system.

as the ASTRA program. Considering the possibility of formation of multilayer structures, the method described in [8] intended for layer-by-layer analysis and implying the existence of local equilibrium in each layer was used. The following conditions were selected:

- the total pressure in the reaction space that is mainly determined by residual air pressure is close to 10^{-5} Pa and constant;
- the temperature is 500 K;
- the ratio $\text{SiO}_2 : \text{Al}$ linearly grows from 0% on the air – aluminum interface to 100% on the aluminum – silicon oxide interface.

It follows from the results of the performed calculations (Fig. 2) that aluminum in fact partly reduces silicic oxide on the $\text{SiO}_2 - \text{Al}$ boundary to metallic silicon, also forming substantial quantities of Al_2O_3 and Al_2SiO_5 (up to 58 and 30%, respectively). It is interesting that reactions with air also produce the impurity Si_3N_4 on the $\text{SiO}_2 - \text{Al}$ interface and the impurity AlN along the total depth of aluminum film.

We investigated two samples of different thickness (300 and 120 nm) obtained under different spraying conditions. The studies using a scanning probe microscope demonstrated that films are discontinuous and consist of spheroid structures. Small “spheres” of diameter about 20 nm merge into larger ones. The diameter of large structures is about 50 nm, and the height 3 nm. The size of discontinuities (depressions)

reaches 250 nm, and their depth is about 15 nm. The film compositions are listed in Table 1. The composition of the silicon-oxygen-aluminum compound in the thinner film corresponds to $\text{SiO}_2 \cdot 1.5\text{Al}_2\text{O}_3$ and in the thicker film to $\text{SiO}_2 \cdot 2.5\text{Al}_2\text{O}_3$. In contrast to gold and copper films, unoxidized silicon is observed on the Al – SiO_2 interface.

Thus, no chemical bonds were found between the metal film and the substrate on the gold – quartz glass interface. The thermovacuum precipitation of copper is accompanied by its oxidation to CuO and Cu_2O . Copper silicate is registered on the copper – quartz glass interface. In magnetron spraying of aluminum, aluminosilicates are formed as well ($n\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), in addition to metallic aluminum and aluminum oxide. As the film increases, the content of aluminum oxide in the compound becomes higher.

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